16.4: The Nernst Equation

> ### ◐ Learning Objectives
>
> Make sure you thoroughly understand the following essential ideas. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.
>
> - The Nernst equation relates the effective concentrations (*activities*) of the components of a cell reaction to the standard cell potential. For a simple reduction of the form $M^{n+} + ne^- \rightarrow M$, it tells us that a half-cell potential will change by $59/n$ mV per 10-fold change in the activity of the ion.
> - Ionic concentrations can usually be used in place of activities when the total concentration of ions in the solution does not exceed about about $0.001 M$.
> - In those reactions in which H^+ or OH^- ions take part, the cell potential will also depend on the pH. Plots of *E vs.* pH showing the stability regions of related species are very useful means of summarizing the redox chemistry of an element.

The *standard cell potentials* we discussed in a previous section refer to cells in which all dissolved substances are at unit *activity*, which essentially means an "effective concentration" of 1 M. Similarly, any gases that take part in an electrode reaction are at an effective pressure (known as the *fugacity*) of 1 atm. If these concentrations or pressures have other values, the cell potential will change in a manner that can be predicted from the principles you already know.

Cell Potentials Depend on Concentrations

Suppose, for example, that we reduce the concentration of Zn^{2+} in the Zn/Cu cell from its standard effective value of 1 M to an to a much smaller value:

$$Zn(s)|Zn^{2+}(aq, 0.001\ M)||Cu^{2+}(aq)|Cu(s) \tag{16.4.1}$$
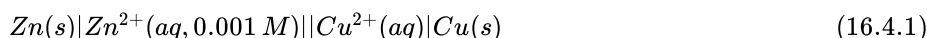
This will reduce the value of Q for the cell reaction

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s) \tag{16.4.2}$$

thus making it more spontaneous, or "driving it to the right" as the *Le Chatelier principle* would predict, and making its free energy change ΔG more negative than $\Delta G°$, so that E would be more *positive* than $E°$. The relation between the actual cell potential E and the standard potential $E°$ is developed in the following way. We begin with the equation derived previously which relates the standard free energy change (for the complete conversion of products into reactants) to the standard potential

$$\Delta G° = -nFE° \tag{16.4.3}$$

By analogy we can write the more general equation

$$\Delta G = -nFE \tag{16.4.4}$$

which expresses the change in free energy for any extent of reaction— that is, for any value of the reaction quotient Q. We now substitute these into the expression that relates ΔG and $\Delta G°$ which you will recall from the chapter on chemical equilibrium:

$$\Delta G = \Delta G° + RT \ln Q \tag{16.4.5}$$

which gives

$$-nFE = -nFE° + RT \ln Q \tag{16.4.6}$$

which can be rearranged to

$$\underbrace{E = E° - \frac{RT}{nF} \ln Q}_{\text{applicable at all temperatures}} \tag{16.4.7}$$

This is the *Nernst equation* that relates the cell potential to the standard potential and to the activities of the electroactive species. Notice that the cell potential will be the same as $E°$ only if Q is unity. The Nernst equation is more commonly written in base-10 log form and for 25 °C:

$$E = E° - \frac{0.059}{n} \underbrace{\log_{10} Q}_{\text{Applicable at only 298K}} \tag{16.4.8}$$

## Significance of the Nernst Equation

The Nernst equation tells us that a half-cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in a one-electron oxidation or reduction; for two-electron processes, the variation will be 28 millivolts per decade concentration change. Thus for the dissolution of metallic copper

$$Cu_{(s)} \rightarrow Cu^{2+} + 2e^- \tag{16.4.9}$$

the potential

$$E = (-0.337) - 0.0295 \log_{10}[Cu^{2+}] \tag{16.4.10}$$

becomes more positive (the reaction has a greater tendency to take place) as the cupric ion concentration decreases. This, of course, is exactly what the Le Chatelier Principle predicts; the more dilute the product, the greater the extent of the reaction.
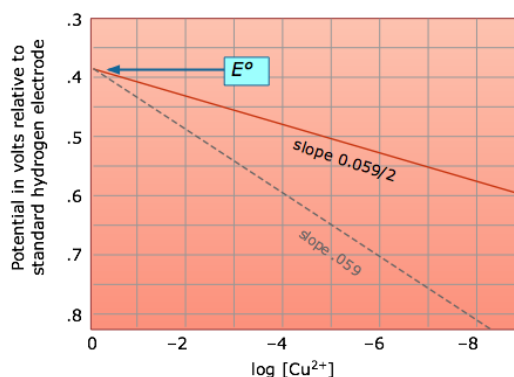

Electrodes with poise

The equation just above for the Cu/Cu^{2+} half-cell raises an interesting question: suppose you immerse a piece of copper in a solution of pure water. With $Q = [Cu^{2+}] = 0$, the potential difference between the electrode and the solution should be infinite! Are you in danger of being electrocuted? You need not worry; without any electron transfer, there is no charge to zap you with. Of course it won't be very long before some Cu^{2+} ions appear in the solution, and if there are only a few such ions per liter, the potential reduces to only about 20 volts. More to the point, however, the system is so far from equilibrium (for example, there are not enough ions to populate the electric double layer) that the Nernst equation doesn't really give meaningful results. Such an electrode is said to be un*poised*. What ionic concentration is needed to poise an electrode? I don't really know, but I would be suspicious of anything much below 10^{-6} M.

📌 The Nernst Equation works only in Dilute Ionic Solutions

Ions of opposite charge tend to associate into loosely-bound ion pairs in more concentrated solutions, thus reducing the number of ions that are free to donate or accept electrons at an electrode. For this reason, the Nernst equation cannot accurately predict half-cell potentials for solutions in which the total ionic concentration exceeds about 10^{-3} M.
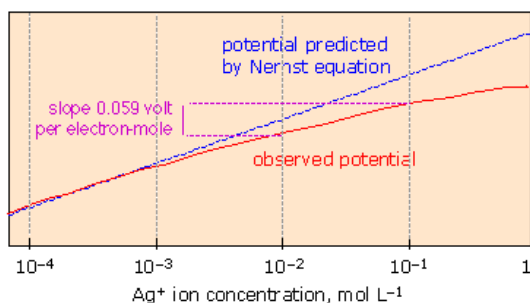
How the cell potential really depends on concentration! The Nernst equation accurately predicts cell potentials only when the equilibrium quotient term Q is expressed in activities. Ionic activities depart increasingly from concentrations when the latter exceed 10^{-4} to 10^{-5} M, depending on the sizes and charges of the ions.

If the Nernst equation is applied to more concentrated solutions, the terms in the reaction quotient Q must be expressed in "effective concentrations" or activities of the electroactive ionic species. The activity coefficient γ) relates the concentration of an ion to its activity a in a given solution through the relation

$$a = \gamma c \tag{16.4.11}$$

Since electrode potentials measure activities directly, activity coefficients can be determined by carrying out appropriate EMF measurements on cells in which the concentration of the ion of interest is known. The resulting Es can then be used to convert concentrations into activities for use in other calculations involving equilibrium constants.

Cell potentials and pH: stability diagrams

As most of us recall from our struggles with balancing redox equations in beginning chemistry courses, many electron-transfer reactions involve hydrogen ions and hydroxide ions. The standard potentials for these reactions therefore refer to the pH, either 0 or 14, at which the appropriate ion has unit activity. Because multiple numbers of H^+ or OH^- ions are often involved, the potentials given by the Nernst equation can vary greatly with the pH. It is frequently useful to look at the situation in another way by considering what combinations of potential and pH allow the stable existence of a particular species. This information is most usefully expressed by means of a E-vs.-pH diagram, also known as a *Pourbaix diagram*.
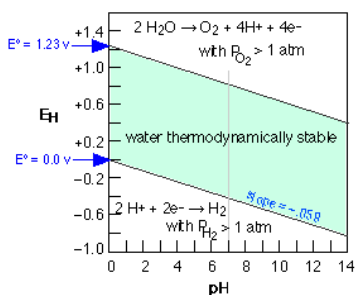

Figure 16.4.2: Stability (Pourbaix) diagram for water. The two E° values shown at the left refer to "standard" conditions of unit H^+ activity (pH=0) and gas pressures of 1 atm. At combinations of pH and E that lie outside the shaded area, the partial pressures of O_2 or H_2 exceed 1 atm, signifying the decomposition of water. The unity partial pressures are of course arbitrary criteria; in a system open to the atmosphere, water can decompose even at much lower H_2 partial pressures, and at oxygen pressures below 0.2 atm. Fortunately, these processes are in most cases quite slow.

As was noted in connection with the shaded region in the figure below, water is subject to decomposition by strong oxidizing agents such as Cl_2 and by reducing agents stronger than H_2. The reduction reaction can be written either as

$$2H^+ + 2e^- \rightarrow H_2(g) \tag{16.4.12}$$

or, in neutral or alkaline solutions as

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \tag{16.4.13}$$
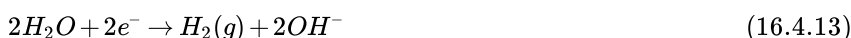
These two reactions are equivalent and follow the same Nernst equation

$$E_{H^+/H_2} = E^°_{H^+/H_2} + \frac{RT}{nF}\ln\left(\frac{[H^+]^2}{P_{H_2}}\right)$$

$$E_{H^+/H_2} = E^o_{H^+/H_2} + \frac{RT}{nF}\ln\left(\frac{[H^+]^2}{P_{H_2}}\right) \tag{16.4.14}$$

which, at 25°C and unit H_2 partial pressure reduces to

$$E = E^° - \frac{0.059}{2} \times 2pH = -0.059\ pH \tag{16.4.15}$$

Similarly, the oxidation of water

$$2H_2O \rightarrow O_2(g) + 4H^+ + 2e^- \tag{16.4.16}$$

is governed by the Nernst equation

$$E_{O_2/H_2O} = E^o_{O_2/H_2O} + \frac{RT}{nF}\ln\left(P_{O_2}[H^+]^4\right) \tag{16.4.17}$$

which similarly becomes $E = 1.23 - 0.059$ pH, so the *E-vs*-pH plots for both processes have identical slopes and yield the stability diagram for water in Figure 16.4.2 This Pourbaix diagram has special relevance to electrochemical corrosion of metals. Thus metals above hydrogen in the activity series will tend to undergo oxidation (corrosion) by reducing H^+ ions or water.


✔ Chlorine in water

Because chlorine is widely used as a disinfectant for drinking water, swimming pools, and sewage treatment, it is worth looking at its stability diagram. Note that the effective bactericidal agent is not Cl_2 itself, but its oxidation product hypochlorous acid HOCl which predominates at pH values below its pK_a of 7.3. Note also that

- Cl_2 is unstable in water except at very low pH; it decomposes into HOCl and Cl^-.
- Hypochlorous acid and its anion are stronger oxidants than O_2 and thus subject to decomposition in water. The only stable chlorine species in water is Cl^-.
- Decomposition of HOCl occurs very slowly in the dark, but is catalyzed by sunlight. For this reason the chlorine in outside swimming pools must be frequently renewed.
- Decomposition of Cl_2 and HOCl by reaction with organic material in municipal water supply systems sometimes makes it necessary to inject additional chlorine at outlying locations.

Each solid line represents a combination of E and pH at which the two species on either side of it can coexist; at all other points, only a single species is stable. Note that equilibria between species separated by diagonal lines are dependent on both E and pH, while those separated by horizontal or vertical lines are affected by pH only or E only, respectively.

✔ Iron

Stability diagrams are able to condense a great amount of information into a compact representation, and are widely employed in geochemistry and corrosion engineering. The Pourbaix diagram for iron is one of the more commonly seen examples.
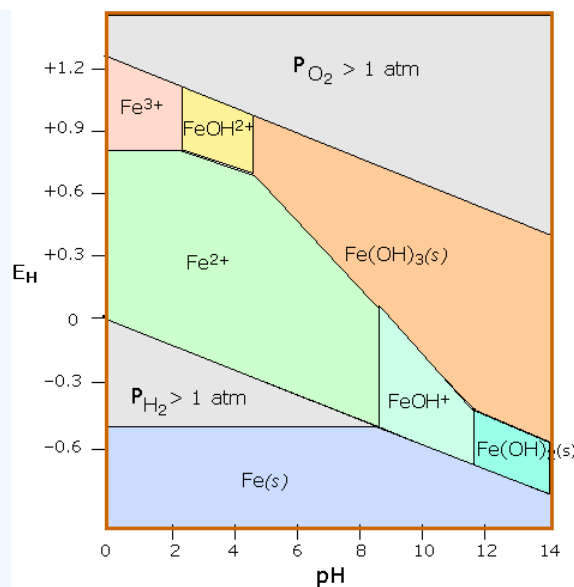
Pourbaix diagram for iron. *Three oxidation states of iron (0, +2 and +3) are represented on this diagram. The stability regions for the oxidized iron states are shown only within the stability region of H₂O. Equilibria between species separated by vertical lines are dependent on pH only.*
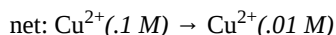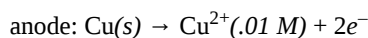
The +3 oxidation state is the only stable one in environments in which the oxidation level is controlled by atmospheric O_2. This is the reason the Earth's crust contains iron oxides, which developed only after the appearance of green plants which are the source of O_2. Iron is attacked by H^+ to form H_2 and Fe(II); the latter then reacts with O_2 to form the various colored Fe(III) oxides that constitute "rust". Numerous other species such as oxides and hydrous oxides are not shown. A really "complete" diagram for iron would need to have at least two additional dimensions showing the partial pressures of O_2 and CO_2.

Concentration Cells

From your study of thermodynamics you may recall that the process

solute *(concentrated)* → solute *(dilute)*

is accompanied by a fall in free energy, and therefore is capable of doing work on the surroundings; all that is required is some practical way of capturing this work. One way of doing this is by means of a concentration cell such as

Cu*(s)* | CuNO₃*(.1 M)* ‖ CuNO₃*(.01 M)* | Cu*(s)*

cathode: Cu^{2+}*(.1 M)* + 2e^- → Cu*(s)*

anode: Cu*(s)* → Cu^{2+}*(.01 M)* + 2e^-

net: Cu^{2+}*(.1 M)* → Cu^{2+}*(.01 M)*

which represents the transport of cupric ion from a region of higher concentration to one of lower concentration.

The driving force for this process is the free energy change ΔG associated with the concentration gradient ($C_2 − C_1$), sometimes known as the free energy of dilution:

$$\Delta G_{dilution} = RT \ln(C_2 - C_1) \tag{16.4.18}$$

Note, however, that Cu^{2+} ions need not physically move between the two compartments; electron flow through the external circuit creates a "virtual" flow as copper ions are created in the low-concentration side and discharged at the opposite electrode. Nitrate ions must also pass between the cells to maintain *electroneutrality*. The Nernst equation for this cell is

$$E = E^\circ - \left(\frac{0.059}{n}\right) \log_{10} Q = 0 - 0.29 \log_{10} 0.1 = +0.285\, V \tag{16.4.19}$$

Note that E° for a concentration cell is always zero, since this would be the potential of a cell in which the electroactive species are at unit activity in both compartments.

$E°$ for a concentration cell is **always** zero,